MOLECULAR DYNAMICS AND THE STRUCTURE OF ASPHALTS AND MODIFIED ASPHALTS AT LOW TEMPERATURES

Daniel A. Netzel, Thomas F. Turner, and Francis P. Miknis
Western Research Institute
365 North 9th Street
Laramie, WY 82070

Jeni Soule and Arland E. Taylor
Chemical and Petroleum Engineering Dept.
University of Wyoming
Laramie, WY 82071

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INTRODUCTION

One important fundamental molecular property of an asphalt, which dictates its temperature dependent performance, is the nature of molecular motions associated with the asphalt molecular components. At any given temperature, the extent of molecular motions depends on the intramolecular configuration of the various asphalt components and the manner in which they interact by intermolecular association. Molecular association tends to restrict molecular motions. Changes in structure and composition brought about by chemical reaction with oxygen as a result of aging also strongly affect overall molecular motion in asphalts through enhanced molecular association, which, in turn, affects the overall long term road performance behavior of asphalts.

On a macro scale the performance behavior of asphalts is manifested in changes in the viscoelastic nature of asphalts, that is, changes in their rheological properties. Thus, an understanding of the molecular dynamics should be helpful in the understanding of the viscoelastic nature of asphalts and in predicting the asphalt composition which optimize binder performance. The molecular mobility can be altered through modification of the asphalt chemically, by the physical blending of two or more asphalts, or the introduction of polymeric materials or other additives to asphalts.

The type and extent of molecular motions can be obtained from hydrogen-1 and carbon-13 nuclear magnetic resonance (NMR) relaxation time measurements. These measurements can provide quantitative information on the molecular structure and degree of molecular motions associated with the hydrogen and carbon types and/or groups in asphalts. Because asphalts are solid-like materials, the molecular motions of interest are low frequency, on the order of 1-50 kHz. The motions of most interest for components of asphalt are methyl rotation, segmental motions (full and/or partial rotation of segments) of the long-chain aliphatic hydrocarbons, and phenyl twisting (torsional oscillation). Figure 1 illustrates the different kinds of motions in a complex asphaltic-like molecule. The structure shown in Figure 1 is a simplification of the "average" structure of the molecules found in asphalt as determined from liquid-state NMR parameters. The structure in Figure 1 consists of polycondensed aromatic carbons with methyl and long-chain hydrocarbon group substituents. The complete "average" structure consists of several methyls and long-chain hydrocarbon groups attached to the aromatic carbon cluster. Generally, there are ~ 30% aromatic carbons and ~ 70% aliphatic carbons in an average "asphaltic" molecule. Not shown in the figure are the heteroatoms which are also of major importance to asphalt chemistry.

EXPERIMENTAL

Solid-state ^{13}C NMR measurements were made using a Chemagnetics 100/200 solids NMR spectrometer operating at a carbon frequency of 25 MHz. Variable contact times experiments were conducted using a 7.5 mm rotor spinning at a rate of 4.5 kHz. Other parameters included a pulse width of 5 μs, pulse delay of 1 s, a sweep width of 16 kHz, 1024 data acquisition points, and between 3000 and 7200 transients. Dipolar dephasing spectra were obtained at a contact time of 1 ms. Low temperatures were obtained using a FTS systems XR Series Air-Jet Sample Cooler. The asphalts were selected from the Strategic Highway Research Program (SHRP) Materials Reference Library.

RESULTS AND DISCUSSION

A stack plot of the dipolar dephasing NMR spectra for asphalt AAM-1 at -45°C is shown in Figure 2. These spectra illustrate the chemical shift position of the different carbon types and clearly show the different relaxation rates at -45°C for the different carbon types. The aromatic carbon region (110-150 ppm) is resolved into quaternary (C, ~ 130-150 ppm) and tertiary (CH, 110-130 ppm) carbon types. The tertiary carbon signals decay much faster than the quaternary carbons. At a dephasing time of 160 μs, the only remaining aromatic carbons are the quaternary carbons which span

the region from 110-150 ppm. Thus, it appears that about 50% of total aromatic quaternary carbons are hidden under the tertiary carbon peak at a dephasing time of 1 μs which approximates a standard cross-polarization experiment. The amount of quaternary carbons dictates the size of the aromatic cluster. Thus, a simple integration of the aromatic region will underestimate the total aromatic quaternary carbons.

The rate of change of the aliphatic carbon types is quite dramatic. Almost all of the methine (CH) and methylene carbons (CH_2) (30-50 ppm) have decayed after a dephasing time of 80 μs. In addition, the sharp methylene peak at 32 ppm decays much faster than the methylene shoulder at 30 ppm. The decays of the methyl carbons (15-30 ppm) are much slower than the other carbon types.

The methyl (CH_3) carbons attached to aromatic rings and branched to a linear main-chain hydrocarbon have resonance peaks in the region of 20-30 ppm. These methyl carbons decay faster than the terminal methyl carbons (15 ppm) of a long chain hydrocarbon. The longer relaxation rates for the two methyl carbon types relative to the methylene and methine carbons are due to the faster rotation motions of the methyl carbons compared to the much slower segmental motions of the methylene and methine carbons. It should be noted that the branched methyl carbons decay faster than the terminal methyl carbons indicating that the branched methyl carbons are rotating slower because of hindrance to rotation than the terminal methyl carbons.

$T_{1\rho}{}^H$ of Asphalts and Modified Asphalts

The hydrogen rotating-frame spin-lattice relaxation time constants ($T_{1\rho}{}^H$) have been used as a probe to study the structure of polymer blends.[1,2] The $T_{1\rho}{}^H$ values are determined by the rate of hydrogen spin-diffusion throughout the sample, which in turn depends upon the homogeneity of the blends and extent of molecular motion.

Figure 3 shows the NMR variable contact time CP/MAS data for Conoco Denver Asphalt and the asphalt modified with 2% Elvaloy® AM (an ethylene acrylate copolymer). The $T_{1\rho}{}^H$ values are derived from the slope of the lines between contact times of 0.5 and 6 ms. The $T_{1\rho}{}^H$ for the Conoco asphalt at 23°C was found to be 1.34 ms and for the 2% Elvaloy AM® modified asphalt the $T_{1\rho}{}^H$ value was found to be 0.92 ms. The smaller relaxation time for the modified asphalt suggests that the correlation time for molecular motion is faster. That is, the overall molecular motions within the asphalt were increased at 23°C. With the limited data, it appears that the modified asphalt is a homogeneous blend based on the fact that only one $T_{1\rho}{}^H$ value represents the data.

Figure 4 shows the variable contact time CP/MAS data for Cenex asphalt (a Wyoming AC-20 asphalt) and the asphalt modified with 3% Butonal® NS175 polymer (a cold polymerized anionic styrene-butadiene dispersion). The $T_{1\rho}{}^H$ values for the asphalt and modified asphalts were found to be 1.41 and 1.09 ms, respectively. Based on the smaller relaxation time for the modified asphalts, the molecular motions were enhanced at 23°C. There is evidence that a second $T_{1\rho}{}^H$ could be fitted to the data suggesting therefore that two domains exist in the asphalts. Additional data will be needed to confirm the observation.

The conclusion of enhanced molecular motions (as suggested from the $T_{1\rho}{}^H$ measurements) for the modified asphalts was limited to one temperature (23°C). To fully understand the dynamic behavior of the polymer modified asphalts, measurements must be made over a range of temperatures. The next section describes the methodology used to quantify the extent of molecular motion in asphalts over a temperature range from +20 to -45°C.

Molecular Mobility in Asphalts at Low Temperature

An important feature in the NMR spectra of any material is the increase in the signal-to-noise ratio as the temperature is decreased. The increase in the signal is due to the difference in the population of nuclear spins in the ground state relative to a higher energy state. That is, as the temperature is lowered, the number of spins increases in the ground state increasing the spin differences between the energy states resulting in an increase in the intensity of the NMR signal. The increase in signal can be predicted from the Boltzmann distribution equation and nuclear spin theory. The total spin magnetization, M_o, at any given temperature is given by equation 1.[3]

$$M_o = N\gamma^2\hbar^2H_o/4kT \qquad (1)$$

where:

N = The number of spins in the sample
γ = gyromagnetic ratio of carbon
$\hbar$ = Planck's constant divided by 2π
Ho = Static magnetic field
k = Boltzmann constant
T = Temperature

Because the carbon-13 magnetization is proportional to the NMR spectral integrated area of the carbon moiety of interest ($M_o \propto A$), the relative increase in carbon magnetization (integrated signal area) can be obtained from the ratio of the two temperatures at which the NMR spectra were obtained (Eq. 2).

$$A_2/A_1 = T_2^{-1}/T_1^{-1} \quad (2)$$

Sullivan and Maciel[4] used equation 2 to show that the increase in the NMR signals for Powhatan #5 coal at temperatures below 21°C is due only to the Boltzmann factor (ratio of the absolute temperature). Coal is a very rigid solid without any apparent or significant molecular motion in the range of 10 to 50 kHz throughout the low temperature range. Because of the lack of molecular motion in coal, the dipolar interaction of the carbons and hydrogens in a cross-polarization experiment is very efficient, whereby, most of the carbons are observed at all temperatures and the increase in signal intensity in coal with decreasing temperature is due only to the Boltzmann factor. Figure 5 shows the change in the CP/MAS spectra of asphalt AAA-1 obtained at temperatures of 20 and -45°C. For the same set of conditions, the signal-to-noise ratio in the NMR spectrum at -45 is considerably better than for the spectrum taken at 20°C. Note also that the signal of the methylene carbons (32 ppm) at -45°C is greatly enhanced relative to the signal at 20°C. The signal enhancement is greater than that predicted by the Boltzmann Factor.

Table I lists the relative signal enhancement, A_{max} (t) / A_{max} (20°C), normalized to 20°C data, for the aliphatic carbons in asphalts AAA-1, AAB-1, and AAM-1 at 20, 0, -10, -20, -30, and -45°C. Also given in the table is the theoretical signal enhancement (T^{-1}/T^{-1}_{293}) expected based upon the ratio of temperatures relative to 20°C (293K). The maximum signal for aliphatic carbons was obtained at a contact time of 0.22 ms (independent of temperature). Figure 6 shows the NMR molecular-mobility/temperature profile plots of the aliphatic area ratios as a function of temperature for the three asphalts. Also shown in Figure 6 is the plot of the theoretical relative signal enhancement as a function of temperature based upon the Boltzmann spin population distribution relative to 20°C.

The ratio of the integrated areas for the aliphatic carbons of the three asphalts differ significantly from coal and from the theoretical signal enhancement due to the Boltzmann factor. These differences are the result of extensive molecular motions in asphalts which prevents effective cross-polarization of the carbon and hydrogen spins. However, as the temperature decreases, the molecular motion decreases, the molecular structure of asphalt becomes more rigid-like, the cross-polarization mechanism becomes more effective and, thus, more carbons are observed resulting in an increase in the integrated area ratio with decreasing temperature. Thus, the area ratio can be defined as a molecular rigidity parameter. That is, as the temperature decreases, the molecular structure becomes more rigid-like.

Asphalt AAA-1 shows a greater enhancement of the aliphatic carbon NMR signal over the temperature range from +20 to -45°C than asphalt AAB-1 which, in turn, shows a greater enhancement than asphalt AAM-1. The greater the relative enhancement at any given temperature the more molecular motion involved for the asphalts. Thus, the extent of segmental and rotational motions of the aliphatic carbons in the asphalts can be ranked as follows: AAA-1 > AAB-1 > AAM-1. This ranking is in the same relative order as the glass-transition temperature, viscosities, and various other rheological properties. As shown in Figure 6, for asphalt AAA-1, the relative signal intensity continues to increase after -45°C. A part of this increase is due to the increase in the Boltzmann factor for the rigid-like carbons. In addition, the signal is expected to increase until the motions due to the presence of a significant amount of methyl rotation and some residual main-chain segmental motions of the aliphatic carbons are stopped. Much lower temperatures will be needed to stop most of these molecular motions. The data for asphalt AAM-1 shows a decrease in signal after -30°C. It has not yet been established whether or not the signal will continue to decrease after -45°C (due to temperature effects on other relaxation mechanisms which can affect the cross-polarization rate) or continue rising at a rate dictated by the Boltzmann factor.

The distinction among asphalts based upon the extent of molecular motions over the temperature range of 65°C for the aliphatic carbons suggest that asphalts modified with small percent of rubber or polymers may be amenable to this NMR technique. In addition, the NMR mobility/temperature profile methodology may be useful to study the rate of oxidation as it affects the motions of the aromatic and/or aliphatic carbons.

The NMR molecular-mobility/temperature profile plots of the asphalts follow qualitatively, but inversely, their DSC thermograms throughout the glass-transition region. The NMR plots describe the change in molecular mobility (molecular dynamics) with changing temperature, whereas, the DSC thermograms measure the changes in the thermal energy (molecular energetics) associated with molecular transitions with changing temperature. Both NMR and DSC data can be expressed using

a cumulative-Gaussian equation. A modified form of the equation was used to fit the NMR data shown in Figure 6 (see equation 3):

$$\rho = A_t/A_{20°C} = 0.5\rho_o\ (1 + erf\ [(t - T_{NMR})/(2^{0.5}\sigma)]) + 293.15/(273.15 + t) \quad (3)$$

where:

ρ	=	relative signal enhancement (A_t / $A_{20°C}$)
ρ_o	=	maximum change in relative signal enhancement
t	=	temperature, °C
T_{NMR}	=	Inflection point temperature, °C
σ	=	standard deviation of the distribution
erf	=	error function

The term, 293.15/(273.15 + t), applies the Boltzmann factor to the fit of the data. The coefficients (ρ_o, T_{NMR} and σ) in equation 3 for the aliphatic and aromatic carbons in the three asphalts are given in Table II. Also given are the onset temperatures for molecular motion for the carbon types in each asphalt. The onset temperature was obtained using equation 4.

$$T_{os}^{NMR} = T_{NMR} + (-2\sigma) \quad (4)$$

The standard deviation of the mean (2σ) encompasses 95% of the observed changes in molecular motion.

The NMR inflection point temperatures and the onset temperatures for significant molecular motions of the aromatic carbons are several degrees higher than the aliphatic carbons. That is, upon cooling the motions of the carbon atoms in the polycondensed aromatic rings are slowed down significantly while the long-chain aliphatic carbons and methyl carbons continue to have considerable segmental and rotational motions. In addition, the NMR inflection point temperature and the onset temperatures were found to be higher than the glass-transition temperature and onset temperature measured using DSC. The NMR inflection point temperatures were found to match more closely the defining temperatures of the asphalts.

The increase in the NMR inflection point temperatures and the onset temperatures going from asphalt AAA-1 to AAM-1 is in agreement with their known rheological and performance predictive properties. Asphalt AAA-1 is the softest (considerable amount of molecular motion) of the three asphalts and asphalt AAM-1 the hardest (the least amount of molecular motions). Thus, the softer the asphalt, the lower the temperature needs to be to stop most of the molecular motion.

CONCLUSIONS

Preliminary $T_{1\rho}^{H}$ data on asphalts and polymer modified asphalts suggest that this NMR relaxation technique can be used to measure the extent of the compatibility of the asphalts and polymer on the overall molecular motions of the asphalts. It is the extent of molecular motion which governs many of the rheological properties of the asphalts. NMR molecular-mobility/temperature profile plots of asphalts were found to follow qualitatively their DSC thermograms. Both the NMR inflection point temperature and the onset temperature for molecular motion were found to be higher than the glass transition temperature and the DSC onset temperatures. Because of the high degree of distinction for the different asphalts, the NMR profile plots should be useful in studying the molecular dynamics in modified asphalts.

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Table I. Carbon-13 NMR Aliphatic Carbon Area Ratios for SHRP Core Asphalts AAA-1, AAB-1 and AAM-1 from Variable Temperature Cross-Polarization Experiments

Temperature (t), °C (K)	Temperature Ratio, T^{-1}/T^{-1}_{293}	AAA-1		AAB-1		AAM-1	
		Integrated Area,[a] $A^{Al}_{max}(t)$	Area Ratio, $A^{Al}_{max}(t)/A^{Al}_{max}(20°)$	Integrated Area, $A^{Al}_{max}(t)$	Area Ratio, $A^{Al}_{max}(t)/A^{Al}_{max}(20°)$	Integrated Area, $A^{Al}_{max}(t)$	Area Ratio, $A^{Al}_{max}(t)/A^{Al}_{max}(20°)$
20 (293)	1.00	14.54	1.00	19.19	1.00	26.13	1.00
0 (273)	1.07	24.51	1.69	30.05	1.57	39.33	1.51
-10 (263)	1.11	28.75	1.98	34.99	1.82	46.36	1.77
-20 (253	1.16	35.48	2.44	43.00	2.24	53.67	2.05
-30 (243)	1.20	39.44	2.71	46.67	2.45	57.59	2.20
-45 (228)	1.29	44.75	3.08	52.06	2.71	56.75	2.17

[a] From maximum signal intensity for aliphatic carbons (ct = 0.22 ms)

Table II. NMR Parameters from the Molecular-Mobility/Temperature Profile Plots for the Aliphatic and Aromatic Carbons in Asphalts AAA-1, AAB-1, and AAM-1

Asphalt	Maximum Change in Signal Enhancement, ρ		Inflection Point Temperature, T_{NMR}, °C		Mean Standard Deviation, 2σ, °C		Onset Temperature for Molecular Motion,[a] T_{os}^{NMR}, °C	
	Aliphatic	Aromatic	Aliphatic	Aromatic	Aliphatic	Aromatic	Aliphatic	Aromatic
AAA-1	1.83	1.42	-10.6	-9.5	±38.5	±32.7	-49.1	-42.2
AAB-1	1.44	0.86	-9.1	-7.7	±35.4	±25.9	-44.5	-33.6
AAM-1	0.94	0.61	-2.2	+1.6	±23.9	±19.2	-26.1	-17.6

[a] Based on 2σ (95%) and excluding CH_3 rotation below -50°C.

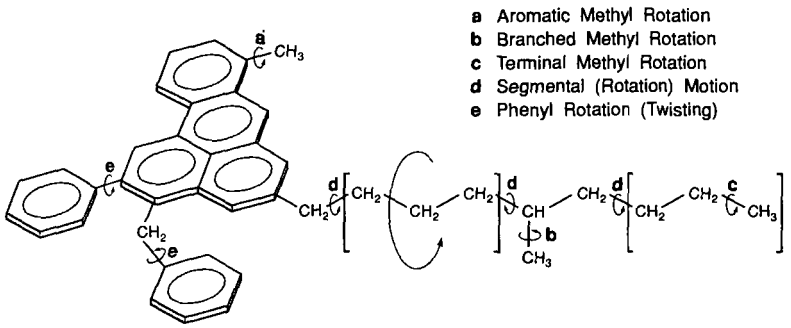

Figure 1. A Simplified "Average" Molecular Structure of Asphalt

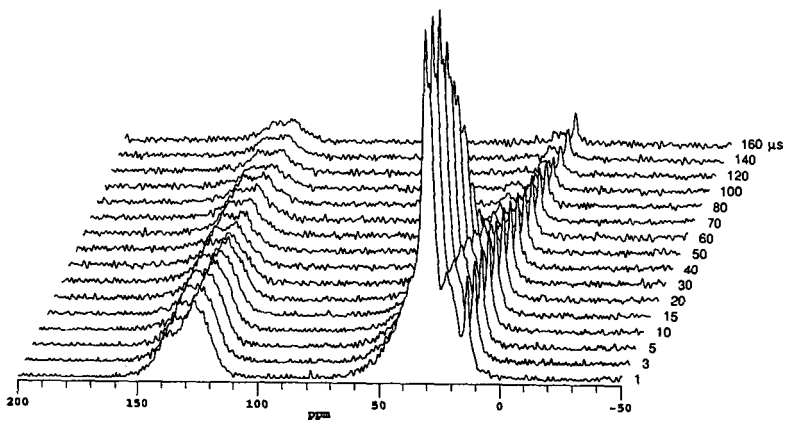

Figure 2. Stack Plot of the ^{13}C Dipolar-Dephasing NMR Spectra for Asphalt AAM-1 at -45°C

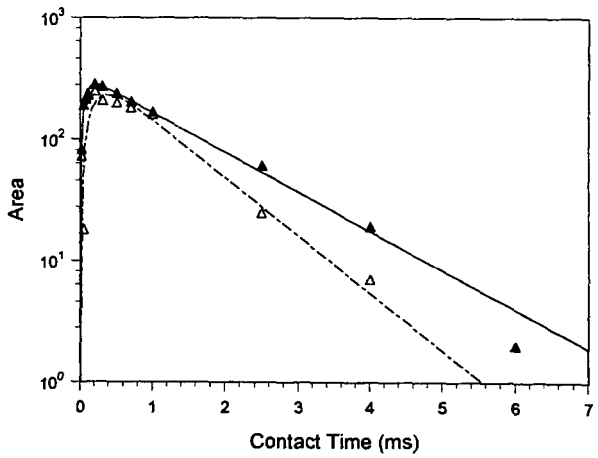

Figure 3. Carbon-13 NMR CP/MAS Variable Contact Time Data at 23°C for Aliphatic Carbons in (▲) Conoco Denver Asphalt, and (△) Asphalt Modified with 2% Elvaloy® AM

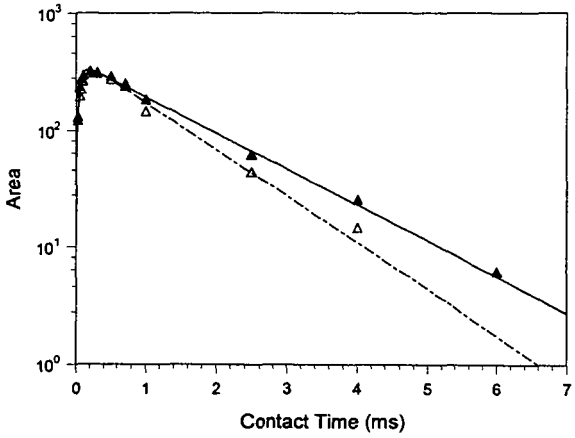

Figure 4. Carbon-13 NMR CP/MAS Variable Contact Time Data at 23°C for Aliphatic Carbons in (▲) Cenex Asphalt and (△) Asphalt Modified with 3% Butanol® NS 175

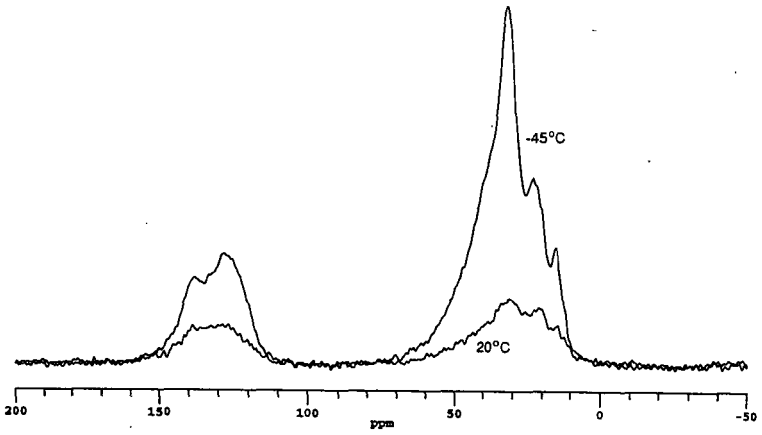

Figure 5. Carbon-13 CP/MAS Spectra of Asphalt AAA-1 at 20 and -45°C

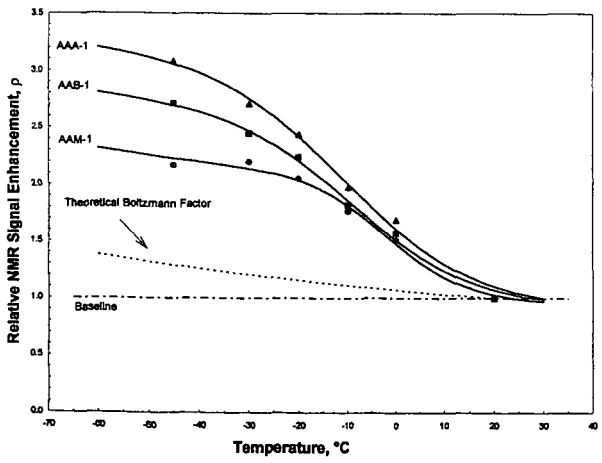

Figure 6. NMR Molecular-Mobility/Temperature Profile Plot for Aliphatic Carbons in Asphalts AAA-1, AAB-1, and AAM-1